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(54) Title: SPRAYABLE ETHYLENE BASED HOT MELT ADHESIVES (57) Abstract This invention relates to sprayable hot melt adhesive compositions comprising an ethylene polymer and a tackifier.		

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Sprayable Ethylene Based Hot Melt Adhesives

Inventors: Michel Faissat and Herman Robberechts

5 Field of the Invention

This invention relates to sprayable hot melt adhesives based upon ethylene copolymers and methods to apply these hot melt adhesives, particularly in disposable
10 packaging and assembly applications and articles produced by such methods.

Background of the Invention.

15 Sprayable hot melt adhesives are desirable for the economic and commercial reasons that they can be thinly, evenly and quickly coated onto a substrate, saving in both time and material, and that they allow better substrate coverage per quantity of adhesive. Typical
20 sprayable hot melt adhesives comprise an amorphous copolymer, generally a butene based copolymer of a styrene based block copolymer, combined with a tackifier. For example, U.S. Patent 4,959,207 discloses sprayable hot melt adhesives of butene copolymers having
25 up to 5.5 to 10 weight % ethylene, tackifier and amorphous diluent having a softening point greater than 90 °C. Similarly, EP 442 045 A2 discloses sprayable hot melt adhesives of amorphous polyalphaolefins having 3 to 75 weight % C₄ to C₁₀ alpha-olefin, 25 to 95 weight %
30 propylene 0 to 20 weight % ethylene. In the past attempts have been made to produce sprayable ethylene α -olefin copolymer based hot melt adhesives. However, these blends were unsuccessful because the polymer would coagulate at the nozzle head or give uneven coating
35 patterns of spots of unequal size rather than a regular even coating pattern. JP- 4180981 A addresses the problem of coagulation at the nozzle head by disclosing

a hot melt adhesives of wax, bivalent phenol stabilizer, partially maleated or fumarated rosin ester tackifier and ethylene copolymer of ethylene mono-carboxylic vinyl ester/acrylic ester and suggesting that they will not
5 clog the nozzle head when sprayed. However, when actually sprayed these hot melt adhesives will not produce a regular even pattern.

Similarly, WO 94 10256 discloses ethylene copolymer
10 blends for hot melt adhesives. However these blends are not suggested for use in spraying applications.

Thus, this invention provides new sprayable hot melt adhesive compositions based upon ethylene copolymers.
15

Summary of the Invention.

This invention relates firstly to sprayable hot melt adhesive compositions comprising: a tackifier and an
20 ethylene polymer having up to 40 weight % comonomer, based upon the weight of the copolymer; a CDBI of 50% or greater; a melt index of 5 or more; and an Mw/Mn of 6 or less and secondly, to a process for spraying ethylene homopolymers and copolymers comprising selecting a hot
25 melt adhesive composition as described above and atomizing, spiral spraying or melt blowing the hot melt adhesive selected onto a substrate.

Detailed Description

30

In a preferred embodiment, this invention relates to sprayable hot melt adhesive compositions comprising: a tackifier, and an ethylene polymer having up to 30 weight % of a comonomer, based upon the weight of the
35 copolymer; a CDBI of 60% or greater; a melt index of 5 or more; and an Mw/Mn of 6 or less.

Preferred ethylene polymers that can be used in the practice of this invention include ethylene homopolymers and copolymers. The copolymers preferably have up to 40 weight %, preferably up to 30 weight %, even more preferably from 5 to 30 weight %, even more preferably from about 10 to about 25 weight %, based upon the weight of the copolymer, of one or more comonomers. Preferred comonomers may be a C₃ to C₄₀ linear, branched or cyclic alpha-olefin. In a preferred embodiment the comonomer is a C₃ to C₂₀ alpha olefin, and in a particularly preferred embodiment the comonomer is butene-1, pentene-1, hexene-1, heptene-1, octene-1, nonene-1, decene-1, undecene-1, dodecene-1, 3,5,5-trimethyl hexene-1, 3-methylpentene-1, 4-methylpentene-1 and the like. Terpolymers of ethylene with two or more of the above monomers are also useful in the practice of this invention.

In another preferred embodiment the ethylene polymers used in this invention have a Composition Distribution Breadth Index (CDBI) of 50% or more, preferably of 60% or more, even more preferably of 70 % or more, even more preferably of 80 % or more. CDBI is a measure of the uniformity of comonomer distribution within a given sample and is measured according to the method described in PCT publication WO 93-03093, published February 18, 1993. A homopolymer has a CDBI of 100%.

In another preferred embodiment the ethylene polymers used in this invention have an Mw/Mn of 6 or less, more preferably 5 or less, even more preferably 4 or less, even more preferably 3 or less, even more between 2 and 1.

In another preferred embodiment the ethylene polymers used in this invention have a melt index as measured by ASTM 1238, condition E, of 5 dg/min or more, preferably

15 dg/min or more, even more preferably 30 dg/min or more, even more preferably between about 100 and 10,000 dg/min.

- 5 In another preferred embodiment, the ethylene polymers of this invention are at least 50 % amorphous, preferably between 60 and 100% amorphous, even more preferably between 70 and 100% amorphous. Percent amorphous content is determined by Differential Scanning
10 Calorimetry measurement according to ASTM E 794-85.

Preferred tackifier that may be blended with the ethylene copolymers described above are those typically used in the art. Examples include, but are not limited
15 to, aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadiene resins, gum rosins, gum rosin esters, wood rosins, wood rosin esters, tall oil rosins, tall oil rosin esters,
20 polyterpenes, aromatic modified polyterpenes, terpene phenolics, aromatic modified hydrogenated polycyclopentadiene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins, hydrogenated terpenes and modified terpenes, and
25 hydrogenated rosin esters. In a preferred embodiment the tackifier is hydrogenated. In another preferred embodiment the tackifier is non-polar. (Non-polar meaning that the tackifier is substantially free of monomers having polar groups. Preferably the polar
30 groups are not present, however if they are preferably they are not present at more than 5 weight %, preferably not more than 2 weight %, even more preferably no more than 0.5 weight %.) In a preferred embodiment the tackifier has a softening point (Ring and Ball, as
35 measured by ASTM E-28) of 80 °C to 140 °C, preferably 100 °C to 130 °C.

The tackifier is typically present at about 15 weight % to about 75 weight %, based upon the weight of the blend, more preferably 30 weight % to 65 weight %, even more preferably 40 weight % to 60 weight %. In a preferred embodiment the tackifier can be a blend of two or more tackifiers. In another preferred embodiment the tackifier comprises a blend of two or more hydrogenated polycyclopentadiene resin. The 5000 series of ESCOREZ™ resins are preferred tackifiers.

The ethylene polymer and the tackifier may be blended together by methods known in the art. For example the ethylene copolymer and the tackifiers can be physically admixed, they can be melt blended, they can be master batched, they can be solvent blended and the like. In one non-limiting example, the polymer and the tackifier are melted in a Z-blade mixer or in a Brabender twin screw extruder and blended under high shear conditions. Their blend components should be chosen so that a final blend viscosity of 20,000 mPaS or less is obtained, preferably 15,000 or less, even more preferably 10,000 or less, even more preferably 8,000 or less even more preferably between 500 and 8000. The range of 500 to 5000 mPa.s at 180°C is ideal for spraying a low coating weight and wide spray pattern (spiral, net like web, or nebulized droplets).

In addition to the polymer and the tackifier, one can add another polymer ("second polymer"). Preferred polymers include any of the polymers described above as ethylene polymers and polymers of ethylene and a polar monomer. The polar monomer is preferably present at up to about 45 weight %, even more preferably up to about 0.5 to about 33 weight %. Preferred polar comonomers may be an ester, a carboxylic acid, an acrylic, and acrylic ester, a vinyl ester or the like. In a preferred embodiment the polar monomer is a vinyl ester

or an alkyl acrylic ester, such as vinyl acetate, acrylic acid, methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, methacrylic acid, ethacrylic acid, and derivatives thereof.

5

The second polymer may be present at up to 50 weight %, preferably 0.1 weight % to 30 weight %. A preferred class of polymer to be added to the composition is an ethylene/propylene/butene terpolymer.

10 Ethylene/propylene/ butene terpolymers are not typically sprayable, however, when blended with the ethylene polymers described above, they can be formed into sprayable compositions. Examples of preferred ethylene/propylene/butene terpolymers are VESTOPLAST™
15 708, VESTOPLAST™750, and VESTOPLAST™408 which are commercially available from Hüls. The ethylene/propylene/butene terpolymer is preferably present at up to 50 weight %, even more preferably at 0.1 weight % to 20 weight %, even more preferably at 0.1
20 weight % to 15 weight %.

Another optional component of the ethylene polymer/tackifier composition is a plasticizer.

Preferred plasticizers include mineral oils,
25 polybutenes, phthalates and the like. Particularly preferred plasticizers include phthalates such as diisoundecyl phthalate (DIUP), diisononylphthalate (DINP), dioctylphthalates (DOP) and the like.

Another optional component of the ethylene
30 polymer/tackifier composition is a low molecular weight product such as wax, oil or low Mn polymer, (low meaning below Mn of 5000, preferably below 4000, more preferably below 3000, even more preferably below 2500). Preferred oils include aliphatic naphthenic oils. Preferred low Mn
35 polymers include polymers of lower alpha olefins such as propylene, butene, pentene, hexene and the like. A particularly preferred polymer includes polybutene

having an Mn of less than 1000. An example of such a polymer is available under the trade name PARAPOL™ 950 from Exxon Chemical Company. PARAPOL™ 950 is an liquid polybutene polymer having an Mn of 950 and a kinematic
5 viscosity of 220cSt at 100 °C, as measured by ASTM D 445.

The blend may then be applied directly to a substrate as a hot melt adhesive or may be sprayed thereon. Spraying is defined to include atomizing, spiral spray controlled
10 fiberization and melt blown techniques. Melt blown techniques are defined to include the methods described in U.S. patent 5,145,689 or any process where air streams are used to break up filaments of the extrudate and then used to deposit the broken filaments on a
15 substrate. In general, melt blown techniques are processes that use air to spin hot melt adhesive fibers and convey them onto a substrate for bonding. Fibers sizes can easily be controlled from 20-200 microns by changing the melt to air ratio. Few, preferably no,
20 stray fibers are generated due to the inherent stability of adhesive melt blown applicators. Under UV light the bonding appears as a regular, smooth, stretched dots pattern. Atomization is a process that uses air to atomize hot melt adhesive into very small dots and
25 convey them onto a substrate for bonding.

The blend may also be applied to a substrate using conventional techniques for applying a hot melt adhesive to a substrate. Examples include hot melt jet nozzle
30 coating, hot melt multiline coating, hot melt slot die coating, hot melt wheel coating, hot melt roller coating, and solvent roller coating.

In a preferred embodiment the blend is applied to a
35 substrate using a spiral spray. Spiral spray is a method used for producing a filamentary spiral application. In one example the hot melt adhesive and

spray air are mixed inside the nozzle, eliminating external influences on the spray pattern. In another example, the hot melt adhesive is drawn into a small fiber by high-velocity air jets. The fiber is then
5 rotated by jets until it contacts the substrate, producing a helical pattern from the single strand of adhesive.

The sprayed hot melt adhesives of this invention can be
10 used for disposable diaper and napkin chasis construction, elastic attachment in disposable goods converting, packaging, labelling and other assembly applications. Particularly preferred applications include: baby diaper leg elastic, diaper frontal tape,
15 diaper standing leg cuff, diaper chassis construction, diaper core stabilization, diaper liquid transfer layer, diaper outer cover lamination, diaper elastic cuff lamination, feminine napkin core stabilization, feminine napking adhesive strip, industrial filtration bonding,
20 industrial filter material lamination, filter mask lamination, surgical gown lamination, surgical drape lamination, and perishable products packaging.

Tests and Materials.

25

CDBI was measured according to the procedure described in PCT publication WO 93-03093, published February 18, 1993.

Melt Index (MI) was measured according to ASTM 1238,
30 condition E (dg/min).

Density was measured according to ASTM D-792 (g/cc).

T-Peel was measured ASTM D1876-72 (20 mm wide test specimens and 2 inch/min (5.08 cm/min) head speed)

Viscosity was measured according to ASTM D 3236 at 180 °C
35 (mPaS)

Penetration was measured according to ASTM D1321-86.

- SAFT (Shear Adhesion Fail Temperature) was measured by adhering a coated polyethylene strip of 25 mm width to stainless steel via press lamination with a contact area of 12.5mm x 25mm, hanging samples in an oven held at 25 °C and suspending a 500 gram weight from the bottom of the strip. The temperature is raised at 0.4 °C/min and the bond failure temperature is measured. The SAFT is the average of three test samples. (°C).
- Hot Shear was measured by suspending a 1000 gram weight from a 25 mm wide strip of polyethylene film coated with the adhesive formulation which is adhered with press lamination to a stainless steel plate with a contact area of 12.5mm x 25mm. The sample is placed in a ventilated oven at 40 °C. Every 30 minutes the temperature is increased by 10°C. Time and temperature are recorded until stress failure occurs. Typically these tests are made and recorded individually to determine the reliability of the holding power. (min, °C)
- Sprayability was measured on a CT 325 Meltex coater under the conditions listed in Example 1. Perfect spiral is shown in figure 1, acceptable spiral is shown in figure 2 and no spiral but unequal spots is shown in figure 3.
- Static shear was measured according to hot shear test set-up described above, but temperature is maintained constant at 50 °C. Time is recorded until stress failure occurs.
- Molecular weights (Mw and Mn) were measured by Gel Permeation Chromatography, unless otherwise noted, using a Waters 150-CV Gel Permeation Chromatograph equipped with a differential refractive index (DRI) detector and polystyrene standards. Polymer samples were dissolved in trichlorobenzene solvent at 165 °C and the solutions were run at 145 °C using three Shodex GPC AT-80 M/S columns in series. This general technique is discussed in "Liquid Chromatography of Polymers and Related

Materials III" J. Cazes Ed., Marcel Decker, 1981, page 207, which is incorporated by reference herein. No corrections for column spreading were employed; however, data on generally accepted standards, e.g. National
5 Bureau of Standards Polyethylene 1475, demonstrated a precision with 0.1 units for Mw/Mn which was calculated from elution times. The numerical analyses were performed using Expert Ease™ software available from Waters Corporation.

10 Melt Flow Rate (MFR) was measured according to ASTM.D 1238 (10 kg, 230 °C)

EXACT™ 4038 is an ethylene butene copolymer having an MI of 125 dg/min, a density of 0.885 g/cc, a butene content
15 of 19 weight percent based upon the weight of the copolymer, an Mw/Mn of 2.06 and a CDBI over 50%, and a crystallinity of about 16%.

EXACT™ 4044 is an ethylene hexene copolymer having an MI of 16.5 dg/min, a density of 0.895 g/cc, a hexene
20 content of 20 weight %, an Mw/Mn of 1.97 and a CDBI over 50 %, and a crystallinity of about 24%.

EXACT™ 4023 is an ethylene butene copolymer having an MI of 35 dg/min, a density of 0.882 g/cc, a butene content of 21 weight %, an Mw/Mn of 2.21 and a CDBI over 50%,
25 and a crystallinity of about 13%.

PARAPOL™ 950 is a liquid polybutene having an Mn of about 950 and a Kinematic viscosity of 220 cst at 100 °C, as measured by ASTM D445.

30 ESCOREZ™ 5380 is a hydrogenated polycyclopentadiene tackifier having a softening point of 85 °C.

ESCOREZ™ 5320 is a hydrogenated polycyclopentadiene tackifier having a softening point of 125 °C.

ESCORENE™ UL 40028 is an ethylene/vinyl acetate copolymer having an MI of 400 dg/min, and a VA content
35 of 28%.

VESTOPLAST™750 is an ethylene/propylene/butene copolymer available from Hüls, having a density of 0.87 and an MV of 70,000.

VESTOPLAST™708 is an ethylene/propylene/butene
5 copolymer available from Hüls, having a density of 0.87 and an MV of 45,000.

DIUP is diisoundecyl phthalate

Meltex CT 325 is a coating machine from Nordson/Meltex.

EP 34-6SD spray head is a spiral spray coating head.

10 IRGANOX™ 1010 is an antioxidant available from Ciba Geigy described in U.S. Patents 3,285,855 and 3,644,482.

Examples

Several different ethylene copolymers were blended with
15 one or more tackifiers according to the following procedure. In a Z-blade mixer with the rotorblades in Z-shape, 204 grams of the ethylene copolymer and 276 grams of tackifying resin were blended incrementally at 180 °C, under nitrogen, until the total volume of the
20 polymer and tackifier were mixed. The components were allowed to mix for 10 minutes, then the parapolymer DIUP, etc, if any, were added. The blend was then mixed for another 50 minutes and poured into a release paper container. Several tests were performed on the various
25 blends according to the procedures described above and the blends were sprayed using a CT 325 Meltex coater under the following conditions:

Melt section temp.: 170°C

Hoze temp.: 175°C

30 Nozzle temp.: 175°C

Air temp.: 200°C

12 notches spiralhead

Nip roll: 1 bar

Brake roll 1: 0-0.5 bar

35 Brake roll 2: 0-0.5 bar

Unwind 1: 0-0.5 bar

Lamination roll 1: 4 bar

Lamination roll 2: 4 bar

Umwind 2: 0-0.5 bar

Cooling Unit: 15-16°C

Webspeed: 125 m/min

- 5 pumpspeed between 40-50 rpm on TACHO to have a coating weight of ± 0.5 g/lm for a spiral diameter of 4-4.5 cm

The polymers, blend components and data are reported in Tables 1 to 4.

- 10 Symbols in the Tables

1 = g/spiral spray ± 4 cm, Adhesive spiral sprayed onto a nonwoven coverstock of thermally bonded polypropylene and then bonded to a polyethylene substrate.

- 15 2 = Adhesive coated onto polyethylene substrate then bonded to another polyethylene substrate.

3 = adhesive meltblown onto a nonwoven coverstock of thermally bonded polypropylene then bonded to polyethylene substrate.

- 20 Perfect blownability means that the adhesive was deposited evenly with the same coating weight left to right on the substrate.

AF = adhesive failure, CF = cohesive failure.

Perfect blownability means that the adhesive was deposited evenly with the same coating weight left to

- 25 right on the substrate.

Perfect spiral means that the spiral is a wide and regular spiral of about 4 cm.

TABLE 1

	Blend A	Blend B	Blend C	Blend D
Exact 4038	50	40	34	-
Exact 4044	-	-	-	40
Escorez 5380	38	43	46	40
Parapol 950	12	17	20	20
Irganox 1010	0.5	0.5	0.5	0.5
Sprayability 4-4.5 cm spiral width	acceptable spiral	good spiral	perfect spiral	no spiral but unequal spots
Sprayability 2-2.5 cm spiral width	perfect spiral	perfect spiral	perfect spiral	no spiral but unequal spots
T-Peel NWC/PE @ R.T. ¹	215 g/spray	475 g/spray	540 g/spray	-
Failure mode	adhesive	adhesive	adhesive	
T-Peel NWC/PE @ 40 °C ¹	40 g/spray	60 g/spray	50 g/spray	
Failure mode	adhesive	adhesive	adhesive	
blend viscosity @ 180 °C (mpas)	13700	6900	3650	22750
Hot shear (min, °C)			11,50 11,50 13,50	
Static shear @ 50 °C (min)			11	
SAFT (°C)			53/53/51	
Penetration @ RT (mm)			3.12	
Penetration @ 40 °C			6.72	
T-Peel PE/PE @ R.T. ² (g/cm)			1285	
Failure mode			cohesive	
T-Peel PE/PE @ 40°C ² (g/cm)			315	
Failure mode			cohesive	

TABLE 2

	Blend E	Blend F	Blend G
Exact 4038	20	15	-
Vestoplast 750			15
Vestoplast 708		35	35
Escorene UL 40028	30	-	-
Escorez 5380	38	38	38
Parapol 950	12	12	12
Irganox 1010	0.5	0.5	0.5
Sprayability 4-4.5 cm spiral width	acceptable spiral	acceptable spiral	no spiral but unequal spots
Sprayability 2-2.5 cm spiral width	perfect spiral	perfect spiral	no spiral/ unequal spots
T-Peel NWC/PE @ R.T. ¹	655 g/spray	480 g/spray	-
Failure mode	adhesive	adhesive	-
T-Peel NWC/PE @ 40 °C ¹	120 g/spray	160 g/spray	-
Failure mode	adhesive	adhesive	
blend viscosity @ 180 °C (mpas)	8400	3920	3000
Hot shear (min, °C)			12,50 11.50 13.50
Static shear @ 50 °C(min)			13
SAFT(°C)			60/60/60
Penetration (mm) @ R.T.			2.02
Penetration (mm) @ 40°C			4.72
T-Peel PE/PE ² (g/cm)@ R.T.			590 AF
Blownability			unaccept- able
T-Peel PE/PE ² (g/cm)@ 40°C			385 AF

TABLE 3

	Blend H	Blend I	Blend J
Exact 4023			24
Exact 4038	34		
Exact 4044		24	
Escorez 5380	23	28	28
Escorez 5320	23	28	28
Parapol 950	20	20	20
Irganox 1010	0.5	0.5	0.5
Sprayability 4-4.5 cm spiral width	perfect spiral	not good	perfect spiral
Sprayability 2-2.5 cm spiral width	perfect spiral	perfect for 1 cm	perfect spiral
T-Peel NWC/PE @ R.T. ¹	875 g/spray	120 g/spray	610 g/spray
Failure mode	adhesive	adhesive	adhesive
T-Peel NWC/PE @ 40 °C ¹	340 g/spray	350 g/spray	400 g/spray
Failure mode	adhesive	adhesive	adhesive
blend viscosity @ 180 °C (mpas)	4500	11720	5660
Hot shear (min, °C)	7,60 7,60 5,60	16,70 18,70	5,60 5,60 5,60
Static shear @ 50 °C(min)	25	298	21
SAFT (°C)	60/60/60	72/72/71	60/59/59
Penetration (mm) @ R.T.	2.73	0.90	2.06
Penetration (mm) @ 40 °C	5.79	2.75	7.14
T-PEEL PE/PE ² (g/cm) @ R.T.	1340 CF	2145 CF	1515 CF
T-PEEL PE/PE ² (g/cm) @ 40°C	425 CF	1100 AF/CF	865 CF
Blownability	perfect		perfect
T-PEEL NWC/PE ³ "Melt Blown" (N/25mm) @ R.T.	2.35 AF		3.50 T
T-PEEL NWC/PE ³ "Melt Blown" (N/25mm) @ 40°C	0.65 AF		2.15 AF

TABLE 4

	Blend K	Blend L
Exact 4038	25	34
Escorez 5320	55	46
Parapol 950	20	20
Irganox 1010	0.5	0.5
Sprayability 4-4.5 cm spiral width	perfect spiral	perfect spiral
Sprayability 2-2.5 cm spiral width	perfect spiral	perfect spiral
T-Peel NWC/PE @ R.T. ¹	600 g/spray	650 g/spray
Failure mode	adhesive	adhesive
T-Peel NWC/PE @ 40 °C ¹	350	280 g/spray
Failure mode	adhesive	adhesive
blend viscosity @ 180 °C (mpas)	2800	5680
Hot shear (min, °C)	13,60 11,60 7,60	16,60 13,60 16,60
Static shear @ 50 °C (min)	>3000	117
SAFT (°C)	66/65/63	62/64/63
Penetration (mm) @ R.T.	1.10	1.70
Penetration (mm) @ 40 °C	5.07	5.38
T-PEEL PE/PE ² (g/cm) @ R.T.	1425 CF	1350 CF
T-PEEL PE/PE ² (g/cm) @ 40 °C	715 CF	660 CF
Blownability	perfect	perfect
T-PEEL NWC/PE ³	0.70 AF	1.80 AF
"Melt Blown" (N/25mm) @ R.T.		
T-PEEL NWC/PE ³	1.25 AF	0.95 AF
"Melt Blown" (N/25mm) @ 40 °C		

All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures. As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby.

Claims:

1. A process for spraying ethylene homopolymers and
5 copolymers comprising selecting a hot melt adhesive
composition comprising: a tackifier and an ethylene
polymer having up to 40 weight % comonomer, based upon
the weight of the copolymer; a CDBI of 50% or greater;
an MI of 5 or more; and an Mw/Mn of 6 or less, and
10 atomizing, spiral spraying or melt blowing the hot
melt adhesive selected onto a substrate.
2. The process of claim 1 wherein the comonomer is a
C₂ to C₄₀ linear, cyclic or branched alpha-olefin,
15 preferably butene, hexene and/or octene, preferably
present at up to about 40 weight %.
3. The process of any of the above claims further
comprising a second polymer.
20
4. The process of claim 3 wherein the second polymer
is an ethylene/propylene/butene terpolymer.
5. The process of claim 3 or 4 wherein the second
25 polymer is present at up to 50 weight percent based upon
the weight of the first and second polymers.
6. The process of any of the above claims wherein
plasticizer is additionally present.
30
7. The process of claim 6 wherein the plasticizer is a
pthalate, preferably diisoundecyl pthalate.
8. The process of any of the above claims wherein an
35 oil or wax is additionally present, preferably the oil
is an olefinic or napthenic oil.

9. The process of any of the above claims wherein a polybutene copolymer having an Mn of less than 2500 is additionally present.
- 5 10. The process of any of the above claims where the tackifier is aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadiene resins, gum rosins, gum rosin esters, wood rosins, wood rosin
10 esters, tall oil rosins, tall oil rosin esters, polyterpenes, aromatic modified polyterpenes, terpene phenolics, aromatic modified hydrogenated polycyclopentadiene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins,
15 hydrogenated terpenes and modified terpenes, and hydrogenated rosin esters.
11. The process of any of the above claims wherein the tackifier is a hydrogenated, linear, cyclic and/or
20 branched pentadiene.
12. The process of any of the above claims wherein the tackifier comprises hydrogenated polycyclopentadiene resin.
25
13. The process of any of the above claims wherein the tackifier comprises a blend of two or more hydrogenated polycyclopentadiene resin.
- 30 14. A process for spraying ethylene/propylene/butene terpolymers comprising:
selecting a hot melt adhesive composition comprising
a ethylene copolymer having up to 40 weight %
35 comonomer, based upon the weight of the polymer; a CDBI of 50% or greater; an MI of 5 dg/min or more; and an

Mw/Mn of 6 or less with a tackifier, an optional plasticizer, an optional antioxidant and the terpolymer.

INTERNATIONAL SEARCH REPORT

International Application No

PC 1/EP 96/03855

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09J123/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,92 12212 (EXXON CHEMICAL PATENTS INC) 23 July 1992 see page 4, line 6 - page 5, line 31 see page 9, line 37 - page 10, line 15 ---	1,2,8-14
Y	WO,A,94 10256 (EXXON CHEMICAL PATENTS INC) 11 May 1994 cited in the application see page 3, line 42 - line 58 ---	1-5,8-14
Y	EP,A,0 442 045 (HUELS CHEMISCHE WERKE AG) 21 August 1991 cited in the application see page 7, line 1 - page 9, line 18 ---	3-5
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- * "A" document defining the general state of the art which is not considered to be of particular relevance
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- * "P" document published prior to the international filing date but later than the priority date claimed

* "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

16 December 1996

Date of mailing of the international search report

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Schmidt, H

INTERNATIONAL SEARCH REPORT

Inter national Application No
PCI/EP 96/03855

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO,A,92 05217 (PLAN B INC) 2 April 1992 see page 5, line 27 - page 6, line 12 see page 9, line 18 - line 35 see page 12, line 1 - page 13, line 32 see page 17, line 26 - line 28 -----</p>	1-14

INTERNATIONAL SEARCH REPORT

International Application No

PC1/EP 96/03855

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		US-A- 5404692	11-04-95
